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# MOLECULAR DYNAMICS STUDY OF SODIUM USING A MODEL PSEUDOPOTENTIAL\*

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## ABSTRACT

The dynamics of sodium is investigated using the coulomb and Born-Mayer interaction augmented by a model pseudopotential to represent the electron interactions including screening, exchange, and correlation. The model parameters were previously determined and have been shown to accurately reproduce experimental equation-of-state, lattice vibration, and crystal phase properties of sodium in the harmonic limit. In this paper the equation-of-state and structural properties are examined in molecular dynamics calculations. The long range effects of the potential are included. Typically, each particle interacts with about 500 neighbors. The calculated equation of state of sodium in the hcp, bcc, and liquid structures is discussed.

## INTRODUCTION

This paper presents the main results<sup>1</sup> of molecular dynamics (MD) calculations for sodium using an interaction potential  $\phi$  derived from pseudopotential theory.  $\phi$  consists of an indirect interaction,  $V_{IND}$ , between pairs of ions, including the effect of electron gas screening, exchange, and correlation, along with the coulomb and Born-Mayer repulsion terms:

$$\phi(r) = \frac{Z^2 e^2}{r} + \alpha e^{-r/\rho} + V_{IND}(r) \quad (1)$$

The indirect interaction is

$$V_{IND}(r) = \frac{1}{\pi^2} \int_0^\infty F(q) \frac{e^{i\mathbf{q} \cdot \mathbf{r}}}{qr} dq \quad (2)$$

where the three empirical parameters in  $F(q)$  and the  $\rho$  and  $\alpha$  in the Born-Mayer term of Eq. (1) were determined by fitting to zero temperature and pressure data and harmonic frequencies of sodium.<sup>2</sup> Figure 1 is a plot of  $\phi(r)$ .

The average kinetic and potential energies of the MD system of ions interacting by way of the effective interaction,  $\phi(r)$ , are not the total system energy. We denote these energies as  $E_K$ , which depends on the detailed structure of the ions. However, the major contribution to the total system energy is given by the volume-dependent

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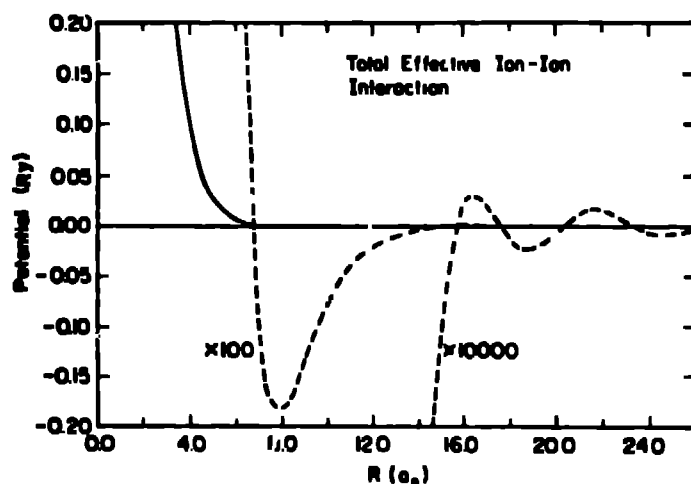


Fig. 1. The total effective ion-ion interaction potential,  $\phi(r)$ .

terms,  $E_v$ .  $E_v$  includes the average electron kinetic energy, exchange, and correlation energy, and  $q = 0$  terms of the pseudopotential. The total system energy is given by

$$E_{TOT} = E_s + E_v .$$

#### SOLID SODIUM

The hexagonal close-packed (hcp) and body-centered cubic (bcc) crystal structures of sodium were simulated by 672-particle MD systems. For each structure we calculated the static ( $T = 0$  K) crystal potential as a function of volume for the range of atomic volumes ( $a_0^3$ ) from 230 to 280  $a_0^3$ . The results were fit to the equation

$$\phi_0(a_0) = p_1 + p_2 a_0 + p_3 a_0^2 + p_4 a_0^3 .$$

The coefficients are given in Table I. The calculated bcc static crystal energy is -0.475 Ry, the zero pressure atomic volume is 255.1  $a_0^3$ , and the bulk modulus is  $5.08 \times 10^{-4}$  Ry/ $a_0^3$ . These values agree within 1% of the observed values. We calculated finite-temperature energies from time averages of the MD kinetic and potential energies to obtain  $E_B$ , to which was added the volume-dependent terms,  $E_v$ .

Table I. Coefficients of the cubic fit of the calculated static crystal potential as a function of atomic volume

Term	bcc	hcp
$p_1$ (Ry)	$-0.310428 \pm 0.011$	$-0.297263 \pm 0.035$
$p_2$ (Ry/ $a_0^3$ )	$(-1.676211 \pm 0.13) \times 10^{-3}$	$(-1.828394 \pm 0.42) \times 10^{-3}$
$p_3$ (Ry/ $a_0^6$ )	$(5.575895 \pm 0.51) \times 10^{-6}$	$(6.161591 \pm 1.6) \times 10^{-6}$
$p_4$ (Ry/ $a_0^9$ )	$(-5.985510 \pm 0.66) \times 10^{-9}$	$(-6.744432 \pm 2.1) \times 10^{-9}$

Typical resulting equation-of-state points are shown for bcc and hcp sodium at an atomic volume of  $256 a_0^3$  in Fig. 2. We notice in this figure the deviation from the harmonic result (the straight lines). The anharmonic contributions to the energy,  $f(\Omega_0, T)$ , defined by

$$E(\Omega_0, T) = \Phi_0(\Omega_0) + 3kT + f(\Omega_0, T) \quad (3)$$

was calculated for hcp and bcc sodium for volumes from 232 to  $270 a_0^3$  (10% compression to 10% expansion) and temperatures from 0 to 400 K. The data was fitted by (see Table II)

$$f(\Omega_0, T) = C(\Omega_0)T^2 \quad (4)$$

### LIQUID SODIUM

The molecular dynamics system melts when the velocities of the particles are great enough to allow them to diffuse away from the perfect lattice positions and form a more random structure. When this liquid state is cooled by artificially removing kinetic energy from the system, it remains in a metastable glassy state to low temperatures. This glassy state may be studied in a manner similar to that described above for the solid to determine its equation of state.<sup>1</sup>

Figure 3 is a plot of the equation-of-state points calculated for bcc and the glassy state of sodium at an atomic volume of  $256 a_0^3$ . The circles

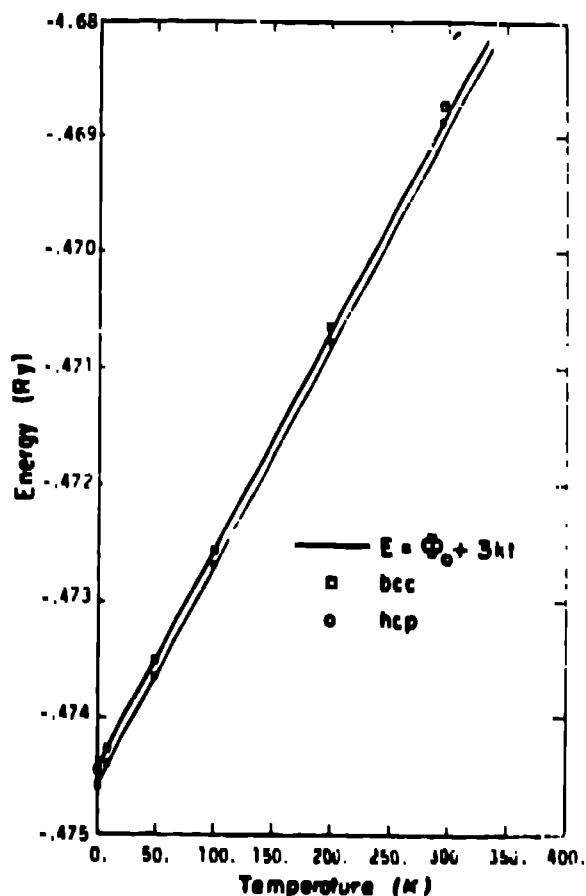


Fig. 2. Total system energy vs temperature for hcp and bcc sodium at an atomic volume of  $256 a_0^3$ .

Table II. Values of the Coefficient  $C(\Omega_0)$

$\Omega_0$ ( $a_0^3$ )	bcc ( $\times 10^{-9}$ Ry/k <sup>2</sup> )	hcp ( $\times 10^{-9}$ Ry/k <sup>2</sup> )
232	$0.908 \pm 0.64$	$1.301 \pm 0.23$
250	$1.012 \pm 0.52$	$1.475 \pm 0.50$
256	$1.250 \pm 0.10$	$1.563 \pm 0.25$
270	$1.350 \pm 0.51$	$2.057 \pm 0.33$

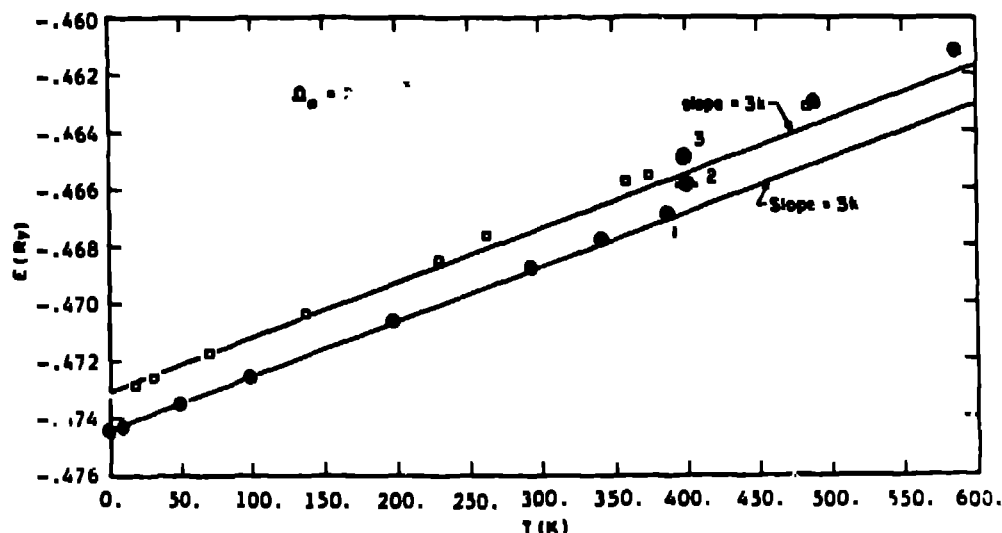


Fig. 3. Equation-of-state points for bcc and liquid sodium. The circles denote points started in the bcc configuration. The squares denote points started in the glassy solid configuration.

that lie on the upper, or liquid, curve represent calculations for which the system melted from the bcc structure.

The points marked 1, 2, and 3 in Fig. 3 represent calculations that had initial temperatures of 400, 450, and 500 K, respectively. Points 1 and 3 have equilibrated to about the same temperature. Point 1 remained on the solid line, point 3 melted and equilibrated at the liquid line, and point 2 formed a partially melted state. We calculated the average mean square displacements from the initial positions,  $\langle \Delta r^2 \rangle$ , for these points. The results are plotted in Fig. 4. After about 400 time units of equilibration, the curve for point 3 attained a constant slope which yielded a diffusion coefficient of  $3.7 \times 10^{-5} \text{ cm}^2/\text{s}$ . The experimental value reported by Faber<sup>3</sup> is  $4.2 \times 10^{-5} \text{ cm}^2/\text{s}$ . The curve for point 1 shows that the particles are not diffusing. The energy difference between the solid and liquid curves of Fig. 3 at 400 K is  $1.7 \times 10^{-3} \text{ Ry/ion}$ , which compares favorably with the experimental latent heat of fusion for sodium of  $2.32 \times 10^{-3} \text{ Ry/ion}$ .

#### DYNAMIC PHASE CHANGE

We have simulated with MD a bcc-to-hcp martensitic phase change in sodium. Both the hcp and bcc MD systems contained 672 particles, with 12 close-packed planes normal to the z-axis, in the same volume but with differently-shaped periodic calculational boxes. We began a calculation of bcc sodium at 50 K and allowed the system to equilibrate for 150 time units. At this point we changed the shape of the periodic box to make it appropriate to the hcp structure. This had the effect of "pushing" the system over a potential hill, forming a face-centered tetragonal (fct) system. The system then relaxed spontaneously to the hcp structure by a slipping of close-packed planes

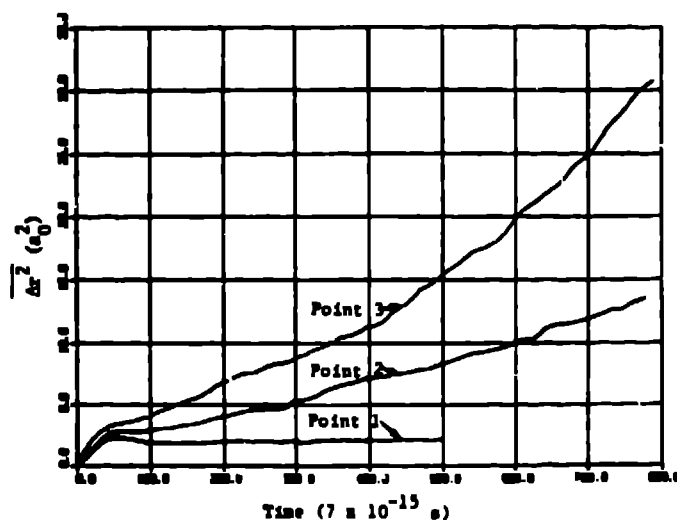


Fig. 4. The mean square displacements vs time for the calculations that produced points 1, 2, and 3 of Fig. 3.

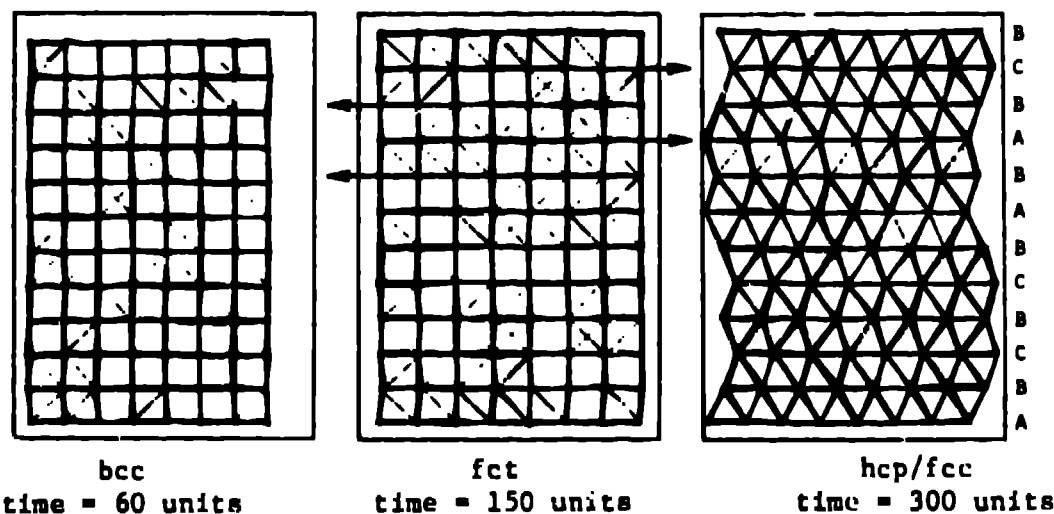


Fig. 5. The molecular dynamics system at three different times during the dynamic phase change. Near neighbors are connected by lines.

relative to one another, as is characteristic of martensitic phase transitions. Fig. 5 shows the molecular dynamics system viewed down rows of atoms with near neighbors connected by lines for the bcc, fcc, and hcp systems. The final equilibrated state of the system is not perfect hcp because stacking faults exist as indicated by the standard A, B, C designations of the relative positions of close-packed planes.

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